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# **Comparative dating of recent peat deposits using natural and anthropogenic fallout radionuclides and Spheroidal Carbonaceous Particles (SCPs) at a local and landscape scale**

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**Abstract:**

Proxy records from recently accumulated peats provide valuable information about past environmental change, but they depend on high quality chronological information to calculate rates and timing of change. However, there is uncertainty in the accuracy and consistency of the methodologies used for dating recent peats. This study compares results from Spheroidal Carbonaceous Particles (SCPs) and natural and anthropogenic fallout radionuclides ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$ ) used to date three replicate cores from three contrasting sites. Data are used to test the consistency of dating techniques within and between sites, and to assess the impact of local conditions on geochronological results.

There is broad consistency in results, but there is also a significant disagreement between dates in a number of cores, both within and between sites. A relatively dry site that had been affected by past burning and erosion showed the greatest consistency between methods and replicate cores. Wetter, less degraded sites showed least consistency. Using patterns of (dis)agreement between dating techniques we assess the potential causes of dating inaccuracy. The data support previous suggestions that  $^{210}\text{Pb}$  is mobile in wetter conditions, and suggests that  $^{241}\text{Am}$  can be considered an increasingly valuable radionuclide. Finally, our data suggest the current estimates for SCP-based ages in the region are incorrect and require further regional calibration.

Using several techniques on replicate cores from three sites in the same area has provided a more robust evaluation of the likely reliability of individual techniques and the processes that may adversely affect them. We conclude that until advances are made in understanding the processes behind the variable quality of SCP and fallout radionuclide dating, using two or more dating techniques will greatly improve understanding of the validity of a peatland chronology, especially in wetter locations.

**Keywords:** Dating recent peat,  $^{210}\text{Pb}$ ,  $^{241}\text{Am}$ ,  $^{137}\text{Cs}$ , Spheroidal Carbonaceous Particles (SCPs), Peat Accumulation.

## 1. Introduction

Biological and geochemical proxies stored in peat deposits can provide valuable information about recent environmental changes, including variability of the peatland environment (e.g. Hendon and Charman, 2004), the broader landscape (e.g. Chambers *et al.*, 1999) and regional changes in climate and pollution loads (e.g. Charman, 2007, Shotyk *et al.*, 1998). Adequate chronological control is a critical part of these studies, especially where rates of change are important, for example in assessing changes in environmental pollutant deposition and rates of carbon accumulation (e.g. Garnett *et al.*, 2000, Turetsky *et al.* 2007). Accuracy of dating is of crucial importance to the validity of these studies and may have a significant impact upon the detection of changes with implications for environmental management. Standard dating techniques, such as calibrated  $^{14}\text{C}$  ages are not generally applicable in recent peats (Belyea and Warner, 1994) and as a result many alternative dating techniques have been developed. Natural and anthropogenic fallout radionuclide (FRN) dating, using geogenic  $^{210}\text{Pb}$  and the artificially-produced  $^{137}\text{Cs}$ ,  $^{241}\text{Am}$  and  $^{207}\text{Bi}$  from nuclear weapons testing (Appleby, 2001) and Spheroidal Carbonaceous Particles (SCPs), pollutants produced from the combustion of fossil fuels (Rose, 2001), are dating methodologies which are commonly applied to peats (e.g. Yang *et al.*, 2001; Garnett *et al.*, 2000; Wieder *et al.*, 1994). 'Bomb-spike' radiocarbon ages are increasingly being used to date recent peats (e.g. van der Linden *et al.*, 2008; Piotrowska *et al.*, 2010), but are often limited by financial constraints. When used together these techniques provide valuable chronologies which can be applied in a number of circumstances (Turetsky *et al.*, 2004). SCPs are very cheap to analyse and can provide several relative dating features, artificial radionuclides provide definite dating peaks for specific events from weapons testing, and fallout  $^{210}\text{Pb}$  is able to produce a continuous chronology for perhaps 100-150 years. These geochronological techniques, however, are not without limitations. FRNs such as  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  are potentially mobile in peats (Urban *et al.*, 1990, Oldfield *et al.*, 1979) and a continuous  $^{210}\text{Pb}$  chronology relies on assumptions about fallout rates and peat accumulation. Dates from SCPs rely on calibration from  $^{210}\text{Pb}$  in mineral sediments where mobility is not an issue and industrial pollution data, and specific changes are not well calibrated for all regions (Rose *et al.*, 1995). As a result, using these techniques does not always prove successful and results from peat cores have been shown to be highly variable (Oldfield *et al.*, 1995).

This study aims to test the techniques commonly employed for dating recent peats by applying FRN and SCP methodologies to replicated cores from three sites with contrasting

local environmental conditions, which are all located within the same blanket mire area. Because the same fallout histories for FRNs and SCPs can be assumed for all cores, we can assess the impact of differing local environmental conditions on the geochronological results.

## **2. Regional Setting**

Peat cores were taken from three blanket peatland sites in the north of Dartmoor National Park, southwest UK. Each site was located in hydrologically and topographically similar areas, but with differing management histories and peat condition (Table 1). A control site represents undisturbed conditions with a high and relatively stable water table. The drained site has a lower and more variable water table and the degraded site is the driest due to on-site erosion and past burning.

INSERT TABLE 1 HERE

## **3. Materials and Methods**

### **3.1 Field sampling**

Along a transect at each site, five 30cm monolith cores were extracted, each 1.5m or 3m apart. Three cores were subject to full SCP and FRN analysis and two were used for SCP dating only. The fully dated cores form the basis for the comparison between dating techniques. Dip-wells were placed at each monolith location to measure approximate water table. Cores 1 – 5 were extracted from the drained site, 6 – 10 from the control site and 11 – 15 from the degraded site.

### **3.2 Natural and anthropogenic fallout radionuclides**

For FRN-based geochronological analysis, each core was cut into 1cm sections which were freeze-dried and weighed. Each core slice was then homogenised and subsamples sealed into 50mm Petri dishes. Sealed samples were stored for 21 days to allow equilibration between  $^{214}\text{Pb}$  and its parent radioisotope  $^{226}\text{Ra}$  prior to measurement by gamma spectrometry (Appleby, 2001). Activity concentrations of the target radionuclides were measured using a low background EG&G Ortec planar (GEM-FX8530-S N-type) HPGe Gamma spectrometry system at the Plymouth University Consolidated Radioisotope Facility. The instrument was calibrated using soil material spiked with certified mixed radioactive standards supplied by AEA Technology Plc. All calibration relationships were derived using EG&G GammaVision software and verified by inter-laboratory comparison tests using

materials supplied by the International Atomic Energy Agency. Total  $^{210}\text{Pb}$  was measured by its gamma emissions at 46.5 keV and its unsupported fallout component calculated by subtraction of  $^{226}\text{Ra}$  activity, which in turn was measured by the gamma emissions of  $^{214}\text{Pb}$  at 295 and 352 keV.  $^{137}\text{Cs}$  was determined by its gamma emissions at 662 keV (with correction for  $^{214}\text{Bi}$  emissions) and  $^{241}\text{Am}$  at 59.2 keV. Resulting activity concentrations were reported with full 2-sigma analytical uncertainty (using ORTEC Gammavision software).

### 3.3 SCPs and charcoal

The SCP approach followed the methodology of Rose (1994). Each sample was weighed and then digested using  $\text{HNO}_3$  for 1 hour 30 minutes, centrifuged at 3000 rpm for 3 minutes, rinsed with deionised water and centrifuged again. As an adaptation to Rose (1994), for each sample a *Lycopodium* tablet was dissolved in 0.5% HCl and added as a known concentration marker after the samples had been thoroughly rinsed. The samples were then transferred to vials, centrifuged and glycerol was added. Samples were mounted on a slide and SCP and charcoal concentrations were counted under a light microscope against a frequency of 50, 75 or 100 *Lycopodium* following the protocols of Rose (2008). SCP and charcoal frequency were calculated as numbers of particles per g dry mass.

## 4. Results

### 4.1 Spheroidal Carbonaceous Particle depth profiles

SCPs were present within each core, and 'take off', 'rapid increase' and 'peak' features outlined in Rose *et al* (1995) and Rose and Appleby (2005) were identified, with the exception of no peak being present in degraded core 15 (Figure 1). Take off and rapid increase features have been identified as relating to  $1860 \pm 25$  and  $1950\text{--}1960 \pm 15$  respectively (Rose *et al*, 1995; Rose and Appleby, 2005). The peak date varies throughout the UK and is identified as  $1970 \pm 5$  in south and central England (Rose and Appleby, 2005).

Dating uncertainty was estimated based on two sources. Firstly, uncertainty as calculated by Rose *et al* (1995) and Rose and Appleby (2005) for the South and Central England region (Table 2) were applied. Secondly, an additional sampling uncertainty was factored in based on the 1cm sampling resolution whereby the dates estimated for a given sample could be considered to be at any point in the range of years represented in the sampling slice.

Peak concentrations varied widely with an average of  $43,130 \text{ SCPs gDM}^{-1}$  and ranged between  $9692\text{--}73,825 \text{ SCPs gDM}^{-1}$ . It is not possible to compare concentrations to lake profiles in the south west region as differing accumulation rates and SCP catchments (e.g. lakes versus peatlands) will affect the total concentration. However, given that SCPs are largely deposited through precipitation (Rose, 2001), and as Northern Dartmoor receives the

highest levels of precipitation in the South West (Met Office, 2010), it is unsurprising that SCP concentrations are relatively high in comparison to the lowland lake sites of the South West on the CARBYDAT (<http://www.ecrc.ucl.ac.uk/index.php/content/view/299/112/>) database.

INSERT TABLE 2 HERE

INSERT FIGURE 1 HERE

#### 4.2 *Fallout radionuclide depth profiles and geochronology*

Fallout  $^{210}\text{Pb}$  inventories for each core (Table 2) are relatively high as would be expected for a rain-fed peatland in granitic terrain and are similar to those presented in Smith *et al* (1997) and MacKenzie *et al* (1997) from both peat and mineral cores. The mean annual  $^{210}\text{Pb}$  fallout in the UK is  $77 \pm 14 \text{ Bq m}^{-2} \text{ year}^{-1}$  per 1000mm of rainfall (Smith *et al.*, 1997). Annual average (1971 to 2000) rainfall for Dartmoor National Park at Princetown is 1974.2 mm (Met Office, 2010) and thus an estimated  $152 \pm 28 \text{ Bq m}^{-2} \text{ year}^{-1}$  of  $^{210}\text{Pb}$  can be inferred, this is in line with the core inventories measured (Table 3). No statistical differences were observed between sites in annual  $^{210}\text{Pb}$  flux levels (one way ANOVA,  $P = 0.251$ ). Annual fluxes for cores within each site type were also within uncertainty of one another, indicating that there was no local variability in atmospheric  $^{210}\text{Pb}$  input. Core control 6 had the highest estimated annual flux ( $197 \pm 33 \text{ Bq m}^{-2} \text{ yr}^{-1}$ ); although this was still within uncertainty of several other cores in other site types.

Depth profiles for  $^{210}\text{Pb}$  showed typical exponential decline with depth in the cores from the degraded site but non-monotonic features were observed in cores from the control and drained sites (Figure 2). Many cores show apparent 'dilution' of  $^{210}\text{Pb}$  activity concentration in the upper layers to approximately 5cm.  $^{137}\text{Cs}$  depth profiles did not exhibit clear peaks in many of the cores (Figure 2). Two of the control cores (6 and 7) and two of the degraded cores (11 and 13) appeared to have higher total  $^{137}\text{Cs}$  inventories, but no statistically significant difference, was observed for the total  $^{137}\text{Cs}$  inventories between cores across the site types (one way ANOVA,  $P = 0.224$ ). Detectable activities of  $^{241}\text{Am}$  were present in seven of the nine cores (Table 3). In two of the seven cores  $^{241}\text{Am}$  was only present for one sample, however in five of the seven cores  $^{241}\text{Am}$  was present in two or more samples (see Figure 3). In these five cores, levels of  $^{241}\text{Am}$  detected were similar at all depths, with no clear peaks in concentration. There was poor coherence between peak  $^{137}\text{Cs}$  and detectable  $^{241}\text{Am}$ .

INSERT TABLE 3 HERE

INSERT FIGURE 2 HERE

The Constant Rate of Supply (CRS) model was used to derive an age depth model from  $^{210}\text{Pb}$  data for each core and apparent accumulation rates following procedures described by Appleby (2001) (Figure 4). The CRS model is considered the most suitable in ombrotrophic peats as  $^{210}\text{Pb}$  inputs are dominated by atmospheric inputs (Turetsky *et al*, 2004; Appleby, 2008; Urban *et al*, 1990). Uncertainty was calculated as in Vile *et al* (1995), from analytical uncertainty and the error propagated from using the CRS model.

#### 4.3 Comparison of SCP and Radionuclide dates

When the independent SCP and  $^{241}\text{Am}$  dates are compared with CRS  $^{210}\text{Pb}$  chronologies, there is a general agreement between dating techniques within the errors (Figure 4). However, there are significant disagreements for a number of profiles and when considered in greater detail, no site type shows a consistent pattern of (dis)agreement except the degraded site (Figure 3). In the degraded site  $^{210}\text{Pb}$  dates are consistently younger than SCP dates, whilst the  $^{241}\text{Am}$  dates for core 11 and 13 are a better match with  $^{210}\text{Pb}$ . In the control site there is a within-error agreement between the  $^{210}\text{Pb}$  chronologies, the SCP dates and  $^{241}\text{Am}$  in cores 6 and 7. However, SCP peaks are slightly younger and take-off dates are older than other dating features. SCP dates from control 8 are inconsistent with the  $^{210}\text{Pb}$  chronology, which may be a result of the poorly defined break points in the SCP profile (Figure 1). The drained site demonstrates a close  $^{210}\text{Pb}$  match with  $^{241}\text{Am}$  in the two cores where it is present. However, the SCP plots do not show a consistent trend. Whilst in cores 1 and 3 the peak ages are a good match with  $^{210}\text{Pb}$ , the SCP start date and take off suggest younger ages than  $^{210}\text{Pb}$ . The drained 5 core SCPs show a similar pattern to the degraded site, with the  $^{210}\text{Pb}$  chronology younger than SCP ages.

Individual dating features may also reveal consistent patterns between dating techniques, if we assume that overlapping error bars indicate agreement between two different age estimates. In each site the SCP peak was either in good agreement (4 cores) with the  $^{210}\text{Pb}$  date or dated younger by the  $^{210}\text{Pb}$  (4 cores), with one date (control 8) being older according to the  $^{210}\text{Pb}$ . The take-off date was mostly in agreement with the  $^{210}\text{Pb}$  chronology (7 cores) and younger at two sites (drained 1 and control 8). The largest individual discrepancies are observed between the start SCP date and  $^{210}\text{Pb}$ , although there is agreement in 3 cores (drained 5, control 8, degraded 14). Most cores show younger ages for SCPs than  $^{210}\text{Pb}$  (4 cores) but two have older SCP ages (degraded 11 and 13).  $^{241}\text{Am}$  showed generally better agreement with the  $^{210}\text{Pb}$  than the SCP dating features, but in all cases the offset tendency of SCPs and  $^{241}\text{Am}$  was in the same direction.



INSERT FIGURE 3 HERE

INSERT FIGURE 4 HERE

#### 4.4 Water table levels

Water tables were measured for eight months between March 2009 and February 2010 at the control and drained sites, and for three months at the degraded site between September 2009 and March 2010. The shorter sampling period was due to logistical problems accessing the site. Differences between water table levels at each site can be seen in Figure 5. The control site has a shallower water table than the drained site (one tailed two sample t-test,  $P < 0.01$ ). The degraded site has a water table which is significantly deeper than both the control (one tailed two sample t-test,  $P = 0.00$ ) and drained site (one tailed two sample t-test,  $P = 0.00$ ) over the period sampled.

INSERT FIGURE 5 HERE

#### 4.5 Bulk Density

Bulk density was recorded at 1cm increments throughout each core profile. Mean bulk density is greatest in the drained site ( $0.14 \text{ g cm}^{-3}$ ), followed by degraded ( $0.12 \text{ g cm}^{-3}$ ) and control ( $0.10 \text{ g cm}^{-3}$ ). Variability in bulk density could indicate a varying accumulation rate, the coefficient of variation (COV) in bulk density calculated from the upper 20cm of each core is greatest in the control site (COV 0.39), followed by the drained (COV 0.27) and is the most stable in the degraded site (COV 0.20).

## 5. Discussion

### 5.1. $^{210}\text{Pb}$ geochronology and hydrological conditions

Dating using the fallout radioisotope  $^{210}\text{Pb}$  is considered one of the most valuable techniques for dating recent sediments (Turetsky et al., 2004). As a natural radionuclide the constant fallout of  $^{210}\text{Pb}$  allows continuous chronologies to be calculated (Urban et al., 1990).  $^{210}\text{Pb}$  dating has been applied in a number of circumstances in peats and is now a well established technique. Despite this, there is still a large degree of uncertainty about the mobility of  $^{210}\text{Pb}$  in peats and thus the validity of age-depth models based solely on it. Geochemically,  $^{210}\text{Pb}$  is a relatively inert radioisotope and its mobility is not an issue in most sediment types (Vile et al., 1999). Recent experimental and fieldwork also suggests Pb is one of the least mobile metals in peat, at least over periods of one to two years (Novak et al, 2011 and Rothwell et al, 2010). However, Damman (1978) found evidence of Pb mobility in peats and hypothesised that this was due to immobile PbS oxidising to form mobile  $\text{PbSO}_4$  and Pb union with dissolved organic matter (DOM) causing fluvial loss, both of which could occur in areas as a result of fluctuating water table. It was suggested this would impact upon the reliability of  $^{210}\text{Pb}$  dating, an assertion which was subsequently corroborated by Oldfield et al (1979) who found poor  $^{210}\text{Pb}$  dating agreement with independent markers in some profiles. As a result, caution is now applied when dating peats using  $^{210}\text{Pb}$ . A number of techniques have been used to establish if mobility is occurring in individual profiles; anomalies in concentration profiles, different  $^{210}\text{Pb}$  total inventories, and disagreement with independent date markers (Belyea and Warner, 1994). These methodologies have resulted in a number of different conclusions to be drawn regarding the mobility of  $^{210}\text{Pb}$  in peat. Here we tested the extent of mobility by replicating analyses in three sites in differing conditions with sites varying from relatively wet with intact surface (control), to drier (drained) and very dry with damaged surface vegetation (degraded). The cores within each site were located less than 3 m apart, and the sites were <20km apart, so we can assume that radionuclide and SCP fallout have been the same across all cores. Three main approaches can be used to assess the likelihood of  $^{210}\text{Pb}$  mobility; 1) comparison of total inventory, 2) irregularities in inventory, and 3) comparisons with independent age markers.

1. A comparison of total  $^{210}\text{Pb}$  inventories to measured fallout can be used to establish if  $^{210}\text{Pb}$  has been mobilised and leached from the system (Urban et al 1990; Smith et al, 1997; Appleby et al, 1997). Urban et al (1990) found that Pb retention was variable (with losses of up to 75% of the input in some instances) and that this was a function of the characteristics of a site; more loss occurred in hollows with high water tables than in hummocks with low

water tables. However, no significant difference is seen between the total  $^{210}\text{Pb}$  inventories between any of the Dartmoor sites (Table 2) despite differences in water table depth. This indicates that there has been no large-scale mobilisation and loss of  $^{210}\text{Pb}$ , due to specific site characteristics, in contrast to the findings of Urban *et al* (1990) and Belyea and Warner (1994). Fallout rates have been shown to be relatively consistent throughout the UK (Smith *et al*, 1997) and these are also in good agreement with those from Dartmoor (Table 2). This indicates that there has not been a significant loss of total  $^{210}\text{Pb}$  at any of the Dartmoor sites, similar to the conclusions of Appleby *et al* (1997) and Smith *et al* (1997).

2. Even minor degrees of mobility could impact upon ages calculated from  $^{210}\text{Pb}$  inventories, as immobility is a major assumption of the CRS model (Ali *et al.*, 2008). Irregularity in expected inventories is a method which Damman (1978) used to identify the movement of elements in peat. It was found that Pb was not mobile in the aerobic acrotelm, but accumulated in the zone of water table fluctuation. Vile *et al* (1999) tested this hypothesis in the laboratory, but no significant change in inventory was found in peats with high or fluctuating water tables and therefore no evidence was found for Damman's sulphide hypothesis. This suggests that the problem may not be as great as first thought, although Vile *et al* (1999) carried out experiments over a period of five months and significant mobility may take longer to occur. Although total inventories of  $^{210}\text{Pb}$  are statistically similar across the sample sites in this study (Figure 2), potential  $^{210}\text{Pb}$  mobility is still an important consideration. It is assumed that each year similar levels of  $^{210}\text{Pb}$  are deposited at the sampling location and inventories will exponentially decrease with depth, if accumulation remains constant (Smith *et al.*, 1997). Deviations from this decrease could be used to indicate  $^{210}\text{Pb}$  mobility (Vile *et al*, 1999 and Damman, 1978), assuming accumulation rates are not variable. Accumulation rates (Figure 3) are calculated in the CRS model, which relies on deviations from the same expected exponential decrease in accumulation (Ali *et al.*, 2008), so using these rates would involve circular reasoning. As a result, the accumulation rates calculated here cannot be relied upon as they are from the same proxy from which  $^{210}\text{Pb}$  mobility is being tested. Independent date markers are therefore required to determine if the irregular  $^{210}\text{Pb}$  profiles in cores 1, 5, 7, and 8 (Figure 2) are due to changing accumulation rates,  $^{210}\text{Pb}$  mobility or a mixture of both as suggested by Smith *et al*, 1997. However, bulk density was more variable in both the control and drained sites, which also both exhibit irregular  $^{210}\text{Pb}$  inventories and are more steady in the degraded site, which also had a more regular  $^{210}\text{Pb}$  inventory. As bulk density can indicate a varying peat accumulation rate, this suggests accumulation rate plays at least some part in the irregular  $^{210}\text{Pb}$  inventories observed within this dataset.

3. The use of independent date markers has been one of the most common sources of evidence for  $^{210}\text{Pb}$  mobility. Although studies which use this technique can only provide an indirect observation of potential  $^{210}\text{Pb}$  mobility (Ali *et al.*, 2008) the methodology is a useful way to validate and constrain  $^{210}\text{Pb}$  dates (Oldfield *et al.*, 1995). However, there is no standardised methodology to define if an independent date agrees well with the  $^{210}\text{Pb}$  CRS date and many studies rely on subjective comparison within individual sequences (e.g. Belyea and Warner, 1994 and Bao *et al.*, 2010). Moreover, independent date markers can be subject to as much error as  $^{210}\text{Pb}$  dating, especially where they involve the onset of industrial Pb pollution (MacKenzie *et al.*, 1997; de Vleeschouwer *et al.*, 2009) or the highly mobile  $^{137}\text{Cs}$  (Urban *et al.*, 1990; Bao *et al.*, 2010, and Ali *et al.* 2008). A number of different conclusions have been reached from comparisons with independent age markers. El-Daoushy *et al.* (1982), Ali *et al.* (2008), Clymo *et al.* (1990), MacKenzie *et al.* (1997), Vile *et al.* (1995), Piotrowska *et al.* (2010), Bao *et al.* (2010) and Appleby *et al.* (1997) all found good agreement with independent markers, whilst Urban *et al.* (1990), Belyea and Warner (1994), Oldfield *et al.* (1979) and Oldfield *et al.* (1995) found some disagreement. Often only a few cores are dated, but studies such as Oldfield *et al.* (1995) and Clymo *et al.* (1990) which use multiple cores and Urban *et al.* (1990) and Belyea and Warner (1994) who recorded site characteristics are more likely to reveal the extent and cause of  $^{210}\text{Pb}$  mobility. A common finding of these studies is that agreement is least consistent in hollows, which are areas of high or fluctuating water table.

Here, we can use the replicated profiles from sites with differing site conditions and history to examine both the relationship between  $^{210}\text{Pb}$  mobility and hydrological conditions, and the consistency of any differences between the sites. It is difficult to identify a regular pattern of agreement or disagreement between  $^{210}\text{Pb}$  and SCP ages across all cores (Figures 3 and 4). Considering the findings of Urban *et al.* (1990) and Belyea and Warner (1994) patterns of agreement in relation to water table level should be prioritised. The driest site (degraded) shows the greatest between-core consistency, with all cores suggesting SCP ages older than the  $^{210}\text{Pb}$  chronologies, especially for the upper peak SCP age. Results from the wetter control and drained sites are more variable, with some cores with SCP ages older than  $^{210}\text{Pb}$  and some that are younger. The results confirm the idea that wetter sites are more likely to give rise to  $^{210}\text{Pb}$  mobility than drier sites and suggest that the mobility is not predictable in terms of direction in the profile.

It can also be noted that in general, there is less agreement between the deepest SCP and  $^{210}\text{Pb}$  dates. In most of the cores, the 1860 SCP date and a number of  $^{210}\text{Pb}$  dates were in regions below the water table or in the zone of water table fluctuation (Figure 4 and Table 3). Although this finding may be related to the large error margins being greatest on SCP and

$^{210}\text{Pb}$  dates at this age, especially in light of recent discussion of detection limits and overestimation of deeper ages (MacKenzie et al., 2011). It may also be as a result of  $^{210}\text{Pb}$  becoming mobilised in areas of high redox, such as the zone of water table fluctuation, as suggested by Urban *et al* (1990) and Belyea and Warner (1994). The fact that total inventories are similar between sites suggests that errors in  $^{210}\text{Pb}$  chronologies may arise as a result of movement of  $^{210}\text{Pb}$  both up and down profiles, but are less likely to lead to significant loss of  $^{210}\text{Pb}$  from the profile.

## 5.2 Considerations for the use of SCPs

High levels of rainfall on Dartmoor lead to high fallout of SCPs, despite the fact that the peninsula of England is less industrialised than other regions of the UK. As a result, the cores within this study all contain countable concentrations of SCPs. In many of the cores, most notably 3, 5 and 6, SCP patterns followed the trends outlined in Rose et al (1995), so that dating features could easily be identified. However, in some profiles, such as cores 7 and 8, the trends did not follow these standard trends, making dating features difficult to identify. These cores have double peaks, or divergence from the expected trend above and below the peak (Figure 1). Similar deviations from the typical patterns can be seen in a number of the SCP profiles published in the CARBYDAT database. Although Rose et al (1995) outline protocols to follow in these circumstances, identifying dating features in profiles which deviate from the expected trend relies upon subjectivity, leading to some uncertainty to the dates allocated. Variable accumulation rates within a core may also cause variable concentration of SCPs. An alternative explanation for variability in SCP trend profiles as a result of local fluctuation in SCP deposition between the three sampling sites is unlikely, given the similarity of the environmental setting and the close proximity of cores within each site. One solution to uneven trends in SCPs is to plot SCP profiles on a cumulative curve up to the peak (Rose and Appleby (2005)). However, as the peak is not present in core 15 and a double peak is present in cores 2, 4 and 10, this technique was not applied here.

Poor SCP profiles may cause some disagreement between SCP dates and other dating features in cores 7 and 8. However, most cores gave a reliable and easily dated trend, but nonetheless did not match the FRN dates. Whilst difference between the profiles suggests that  $^{210}\text{Pb}$  mobility is highest in wetter conditions, some of the difference between SCPs and  $^{210}\text{Pb}$  may be attributable to error in SCP ages, arising from poor calibration of SCP dates in the south west of England. This is supported by the  $^{241}\text{Am}$  dates, which are closer to the  $^{210}\text{Pb}$  dates than the SCPs in two of the three degraded cores (Figure 5) and in drained core 5. SCP records are spatially variable throughout the country (Rose and Harlock, 1998) and peak and take-off dating features occur at different times, due to varying amount and timing

of industrialisation. Rose *et al* (1995) and Rose and Appleby (2005) have brought together a database of SCP profiles and  $^{210}\text{Pb}$  chronologies, ('CARBYDAT' <http://www.ecrc.ucl.ac.uk/index.php/content/view/299/112/>), which identifies differing SCP chronologies across the United Kingdom. Dartmoor falls within the large region of 'the south', but only a few coastal cores from the southwest are used for calibrating SCP ages here, and most of the cores are in the southeast of England. Prevailing southwest winds, the upland location and less industrialisation in the southwest mean that SCP trends for Dartmoor may be different to those in the south east and are therefore poorly calibrated. This could be a cause for disagreement between  $^{210}\text{Pb}$ ,  $^{241}\text{Am}$  and SCP dates observed in figure 4. In further support of this, the southwest SCP dated profiles from the CARBYDAT database from Slapton Ley (on the south Devon coast) and Pinkworthy Pond (on the north coast near Exmoor) have a mid-1980s peak and mid-1960s take off, later than the southern region average dates (Rose *et al* (1995). Given that the most consistent  $^{210}\text{Pb}$  results are from the degraded site and that these and other cores have SCP ages that are apparently too young, we suggest that the mid-1960s and mid-1980s dates are more reliable for Dartmoor than the southern region averages.

### 5.3 Considerations for use of artificial fallout radionuclide markers in peat

Although detectable levels of  $^{137}\text{Cs}$  were present in each of the profiles, clear dating features were not (Figure 2). This is commonly reported in peat studies (Gerdol *et al*, 1994 and Oldfield *et al*, 1995).  $\text{Cs}^+$  is not as strongly exchanged as other cations and hence is mobile in peats, which have high cation exchange capacities (MacKenzie *et al.*, 1997). Moreover, clay is a key binding site for  $\text{Cs}^+$  (Shand *et al.*, 1994), and as ombrotrophic peats contain no clay,  $\text{Cs}^+$  remains mobile. Evidence for mobility is clear in this dataset; detectable  $^{137}\text{Cs}$  concentrations are still present below the 1952 depths dated by SCP dating markers, CRS  $^{210}\text{Pb}$  ages and  $^{241}\text{Am}$  (Figure 2 and Figure 3). This is the date at which  $^{137}\text{Cs}$  was first present as a result of fallout and detectable levels should not occur below this date. Furthermore, peaks in  $^{137}\text{Cs}$  concentration, where present (Figure 2) do not relate to the  $^{241}\text{Am}$  presence (Figure 3). These data provide further confirmation that  $^{137}\text{Cs}$  is not a reliable marker in peats. The fallout radionuclide  $^{241}\text{Am}$  usually is considered a reliable artificial fallout radionuclide in peats, due to its immobility relative to  $^{137}\text{Cs}$  (Appleby *et al*, 1988 and Oldfield *et al*, 1995).  $^{241}\text{Am}$  decays from  $^{241}\text{Pu}$  fallout *in situ* and has been becoming increasingly valuable as a dating tool (Appleby *et al.*, 1991). For example, further decay of  $^{241}\text{Pu}$  was calculated by Appleby *et al.*, 1991 to increase detectable levels of  $^{241}\text{Am}$  between 1990 and 2037 by 24% (Appleby *et al.*, 1991).  $^{241}\text{Am}$  is not widely reported in peat studies and as a result relatively little is known about it in this context. The patterns and variability of  $^{241}\text{Am}$  in these cores may give an indication of its reliability.  $^{241}\text{Am}$  was not

detected in all cores and where present, the levels detected were very low with large detection errors (Table 3). The presence or absence of  $^{241}\text{Am}$  in each core could be as a result of variability in  $^{241}\text{Pu}$  fallout and at levels close to detection limits. Strong peaks of  $^{241}\text{Am}$  with good agreement with other dating techniques have been reported (Smith *et al*, 1997; Appleby *et al*, 1988; Clymo *et al*, 1990; Oldfield *et al*, 1995). Similarly, in this study when  $^{241}\text{Am}$  is dated from the median depth at which it occurs, there is generally good agreement with both SCPs and  $^{210}\text{Pb}$  (Figure 4). A long half life (432 years) and future improvement in detection limits make  $^{241}\text{Am}$  a valuable tool, particularly when  $^{210}\text{Pb}$  is no longer available for the industrial period.

## **6. Conclusion**

This study has provided an example of some of the challenges faced when using methodologies to date recent peats. Although each technique displayed a level of success, it also has identified that each of the methodologies used had a number of uncertainties associated with it. Using multiple techniques has proved a successful approach, as together these techniques are able to provide a coherent understanding of the quality of a chronology. At the very least it is possible to identify profiles where the chronology is most uncertain and distinguish these from profiles which display internal consistency. The replication of cores from three different sites suggests that drier sites provide more reliable  $^{210}\text{Pb}$  chronologies because mobility is reduced. Wetter sites show less predictable patterns of mobility. Until further advances are made in improving understanding the processes behind the variable quality of fallout radionuclide and SCP dates in peats, the use of two or more dating techniques together will greatly improve understanding of the validity of a peatland chronology, especially in wetter locations with water tables close to the surface. Moreover, replication of cores from study sites could be used more extensively to ensure that variability and potential error in peat chronologies is adequately understood in interpretation.

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## Tables

Site	Slope (°)	Elevation (m)	Aspect (°)	Peat condition	Vegetation	Site location (lat, long)
Drained	3.1	496	287	Intact except for infilled shallow drainage ditches	Predominantly vascular plants with some <i>Sphagnum</i>	50.589, -4.008,
Control	2.8	534	244	Intact	Blanket mire vegetation incl. <i>Sphagnum</i> & <i>Eriophorum</i>	50.601, -3.999
Degraded	2.5	577	244	Hagged with small vegetated gullies	Vascular plants	50.645, -3.977

Table 1

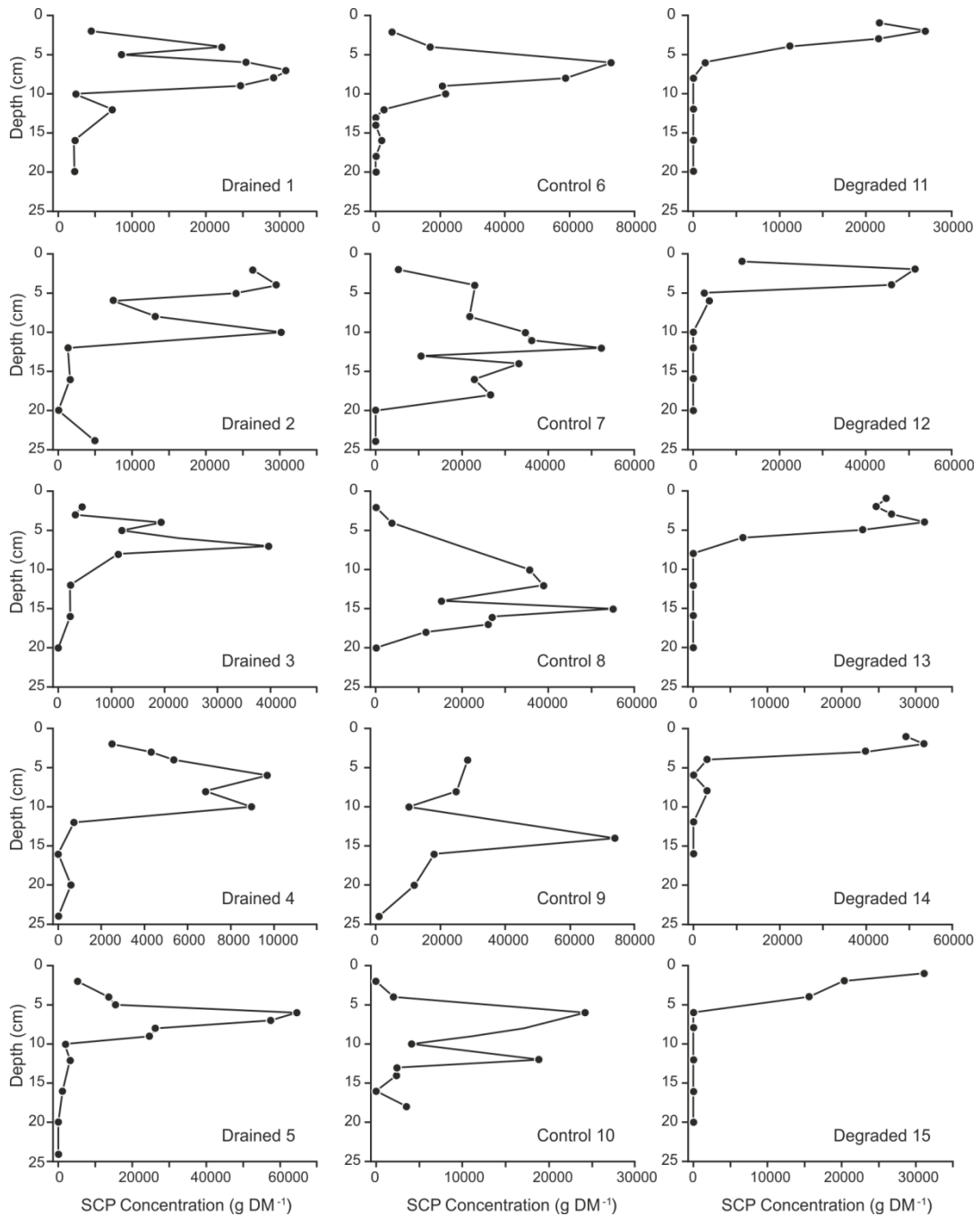
<b>Core</b>	<b>Peak Depth (cm)</b>	<b>1970 Peak Error (years)</b>	<b>1955 Take off depth (cm)</b>	<b>Take off error (years)</b>	<b>1860 Start Depth (cm)</b>	<b>Start error (years)</b>
Drained 1	7	± 9	11	± 28	16	± 44
Drained 2	10	± 12.5	12	± 27	20	± 37
Drained 3	7	± 11	9.5	± 23	20	± 33
Drained 4	6	± 7.5	12	± 24	24	± 33
Drained 5	6	± 9	10	± 23	20	± 31.5
Control 6	6	± 8	11	± 24	18	± 39
Control 7	12	± 9	16	± 29	20	± 49
Control 8	16	± 12.5	18	± 28	20	± 72.5
Control 9	15	± 20	16	± 28	25	± 44
Control 10	6	± 10	10	± 26.5	16	± 49
Degraded 11	2	± 10	5	± 33	8	± 52
Degraded 12	2	± 10	5	± 30	10	± 44
Degraded 13	4	± 12.5	6	± 45	8	± 72
Degraded 14	2	± 11	4.5	± 26	12	± 38
Degrade 15	None unidentifiable				6	± 44

Table 2

<b>Core</b>	<b><math>^{210}\text{Pb}</math> inventory (Bq <math>\text{m}^{-2}</math>)</b>	<b>Annual <math>^{210}\text{Pb}</math> flux (Bq <math>\text{m}^{-2}</math> <math>\text{yr}^{-1}</math>)</b>	<b><math>^{137}\text{Cs}</math> inventory (Bq <math>\text{m}^{-2}</math>)</b>	<b><math>^{241}\text{Am}</math> inventory (Bq <math>\text{m}^{-2}</math>)</b>
Drained 1	5552 $\pm$ 757	173 $\pm$ 24	807 $\pm$ 93	0 $\pm$ 0
Drained 3	4458 $\pm$ 660	139 $\pm$ 20	698 $\pm$ 117	11 $\pm$ 4
Drained 5	5399 $\pm$ 671	168 $\pm$ 21	795 $\pm$ 147	42 $\pm$ 20
Control 6	6326 $\pm$ 1071	197 $\pm$ 33	1459 $\pm$ 198	7 $\pm$ 4
Control 7	4103 $\pm$ 674	128 $\pm$ 21	1066 $\pm$ 131	17 $\pm$ 9
Control 8	4714 $\pm$ 603	147 $\pm$ 19	739 $\pm$ 100	0 $\pm$ 0
Degraded 11	4242 $\pm$ 664	132 $\pm$ 21	1396 $\pm$ 121	26 $\pm$ 12
Degraded 13	4387 $\pm$ 546	137 $\pm$ 17	1335 $\pm$ 99	35 $\pm$ 15
Degraded 14	3488 $\pm$ 555	109 $\pm$ 17	840 $\pm$ 102	15 $\pm$ 6

Table 3

## Figures



**Figure 1**



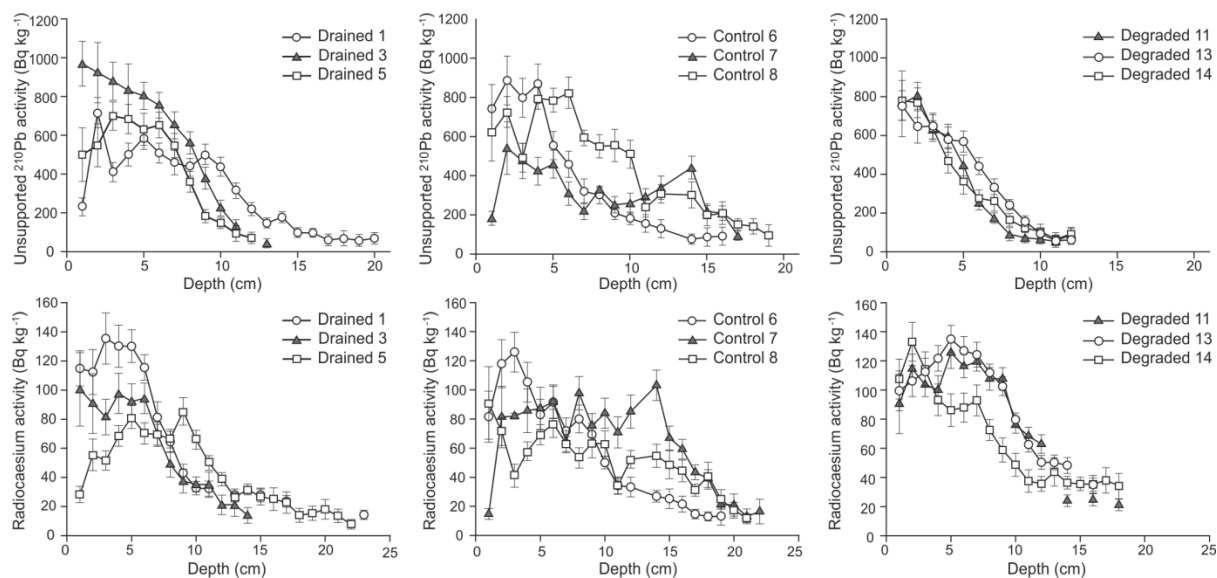


Figure 2

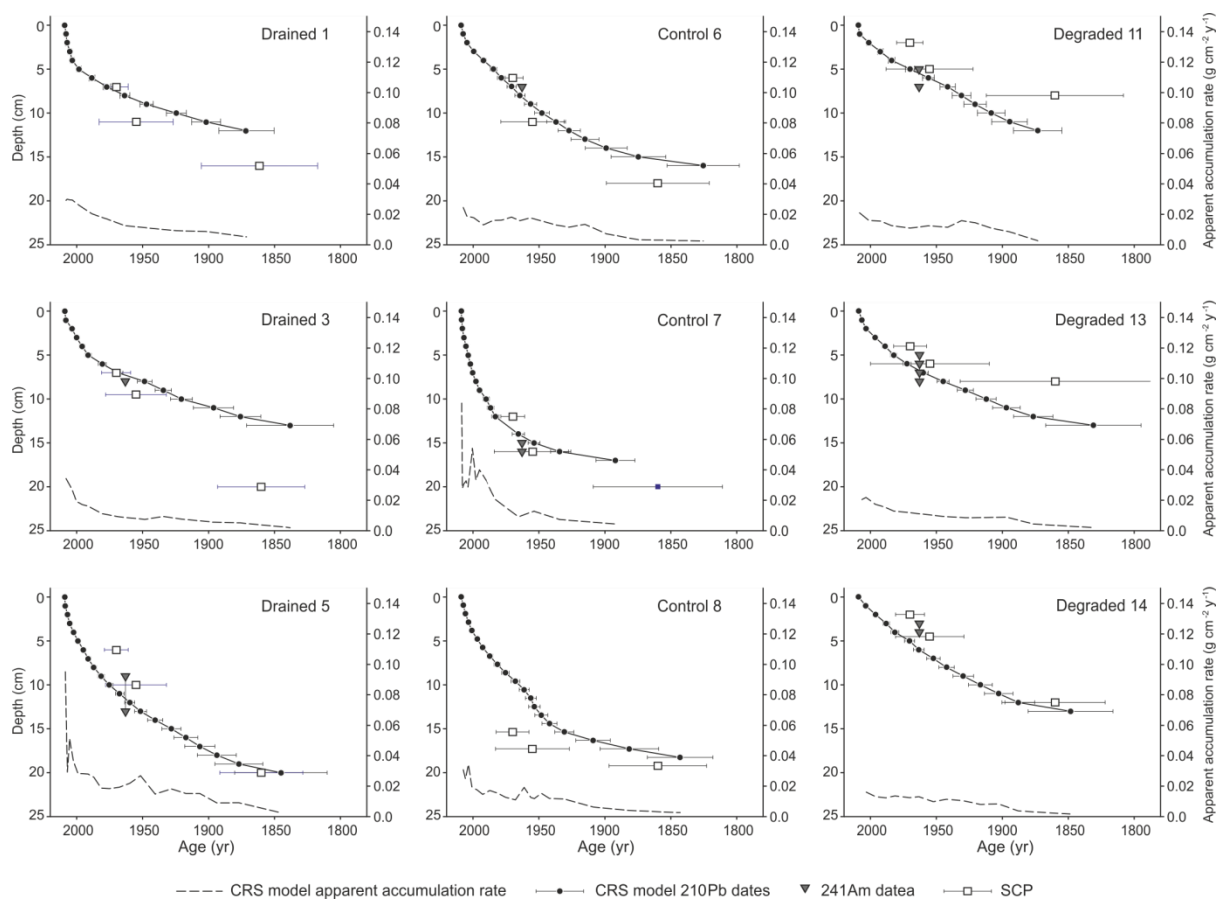
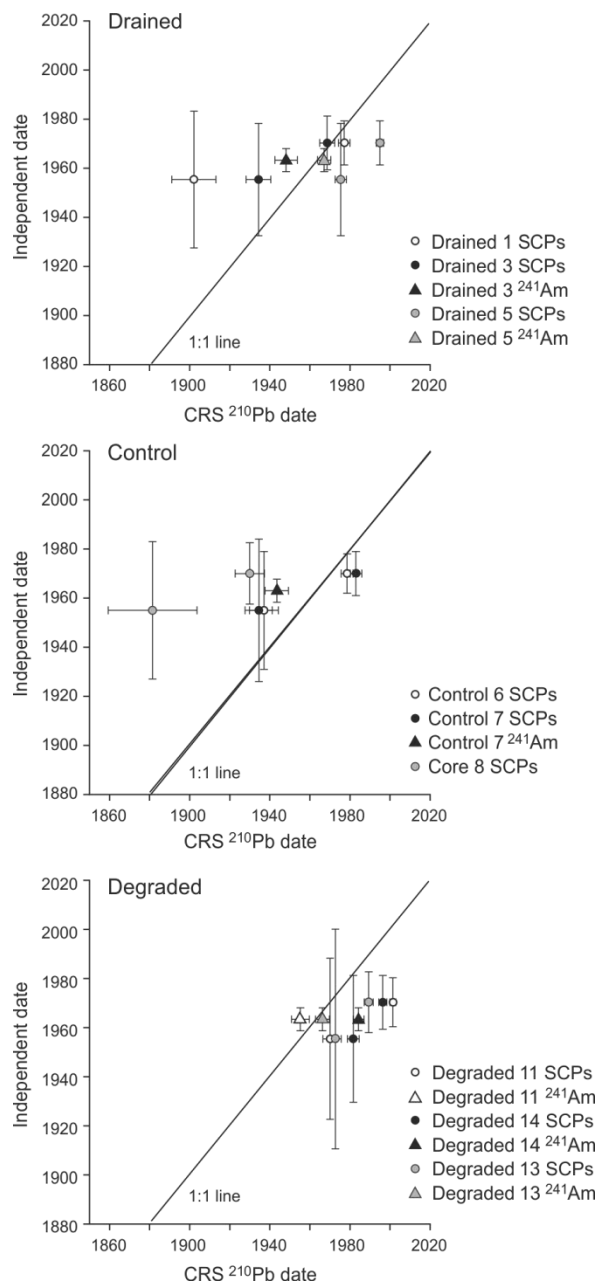


Figure 3



**Figure 4**

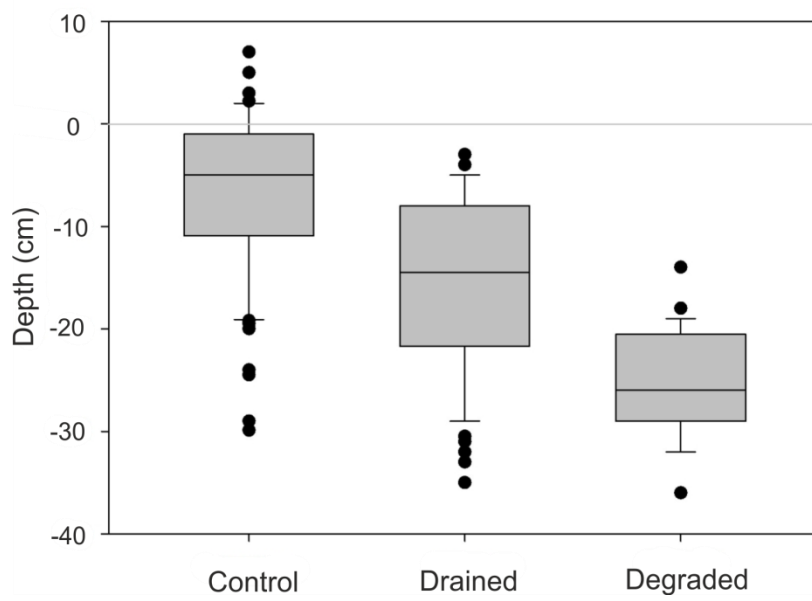


Figure 5